Hydrometallurgical recovery of critical metals from WEEE shredding dust

Marra A.*, Cesaro A. And Belgıorno V.

Sanitary Environmental Engineering Division (SEED), Department of Civil Engineering, University of Salerno, via Giovanni Paolo II, n.132, 84084 Fisciano (SA), Italy

*corresponding author:

e-mail: amarra@unisa.it

Abstract.

The recycling of metals from Waste Electrical and Electronic Equipment (WEEE) can be regarded as a relevant economic opportunity as the industry of electronic devices is a large consumer of both base and special metals. Significant portions of precious metals and rare earth elements contained in WEEE are however lost in recycling treatments, especially through dust stream originating from shredding and other separation steps involved in mechanical processes. The management of this dust fraction concerns both economic and environmental issues as it is currently disposed of in landfill. If the occurrence of hazardous substances is a matter of environmental concern, on the other hand the presence in dust of reasonable concentrations of valuable metals makes this matrix a potential attractive source of secondary materials. Nevertheless, research studies on refining treatments for critical metal recovery from WEEE shredding dust have not been reported yet. The present study aimed at investigating the potential application of refining processes to dust materials originating from a full scale WEEE treatment plant. For this purpose, a chemical leaching process was carried out and the optimization of the operating parameters was discussed. The leaching capacity of selected metals was evaluated and a hydrometallurgical approach was proposed for valuable and critical metal recovery from dust waste.

Keywords: electronic waste, chemical leaching, dust material, precious metals, rare earth elements

1. Introduction

The management of Waste Electrical and Electronic Equipment (WEEE), including end-of-life appliances powered by electricity, is currently a matter of great interest as this waste stream provides the higher generation rate per year (Robinson, 2009) and a wide-ranging source of materials (Tanskanen, 2013). Due to the continuous replacement of obsolete devices with new technologically advanced versions, the generation of WEEE is increasing over time, resulting in an annual global production of around 20–50 million tons (UNEP, 2013). More than 1000 different substances can be found in WEEE (Widmer *et al.*, 2005), including both hazardous components (i.e. heavy metals and flame retardants) and strategic materials as precious materials and rare earth elements (REEs). Rare earths, counting 15 lanthanides plus scandium and yttrium, have been defined as "critical metals" due to both their high demand and great supply risk (Bakas *et al.*, 2014). These elements are widely used in electronic appliances such as audio, video equipment and computers as well as in communications systems, automobiles and military applications (Han *et al.*, 2014). The recycling of REEs from electronic waste could, thus, contribute to the future supply of these elements (Binnemans *et al.*, 2013; Guyonnet *et al.*, 2015). However, the WEEE recycling industry is primarily oriented towards the recovery of base and precious metals while rare earth elements are subjected to great losses during the treatment processes. These losses began in the early stages of the recycling chain, namely the mechanical pre-treatments (Tsamis and Coyne, 2015) which are primarily designed to provide the liberation of metals for their further refining (Cui and Zhang, 2008; Khaliq *et al.*, 2014). Nevertheless, the shredding processes involved in mechanical treatments result unfavorable for the recovery of both precious metals and rare earth elements that are conveyed in the dust stream (Chancerel *et al.*, 2009; Tsamis and Coyne, 2015). Strategic materials are, thus, mainly lost in this fraction which is actually disposed of in landfill, representing a cost for the treatment plants (Bachér *et al.*, 2015). Hydrometallurgical treatments have been considered as an effective alternative to pyrometallurgical processes for metal recovery from WEEE. Whereas pyrometallurgy exploits high temperature processes for the recovery of metals, hydrometallurgy is based on the metal mobilization from the solid matrix via leaching processes followed by its extraction from the liquid solution trough precipitation, solvent extraction, adsorption or ion exchange. Compared to pyrometallurgy, hydrometallurgy provides low capital costs and requires less energy consumption. Moreover, the process offers higher recovery rates as well as easily operating conditions (Cui and Zhang, 2008; Tuncuk *et al.*, 2012). Since hydrometallurgical processes involve chemical lixiviants, the research is currently directed towards the utilization of less toxic agents (Gurung *et al.*, 2013) as well as to the optimization of these processes for the extraction of rare earths from WEEE that is still in its infancy (Peelman *et al.*, 2014). In this background, the goal of the present work was to investigate the application of hydrometallurgical processes on WEEE shredding dust for the extraction of valuable and critical metals. In details, a chemical leaching process developed into two separate steps was proposed in order to selectively recover base metals as well as rare earth elements during the first stage and precious metals in the second one. In the first step, sulfuric acid, widely used for the extraction of base metals from WEEE (Birloaga *et al*., 2013; Oh *et al*., 2003; Yang *et al*., 2011), was tested for the mobilization of rare earths whereas in the second stage thiourea was involved as non-conventional leaching agent for the extraction of gold. The optimization of the factors affecting the leaching process was, moreover, discussed.

2. Materials and methods

2.1. Materials

For this study, WEEE shredding dust was collected at a full scale plant operating in Southern Italy. This facility treats small electronic equipment via mechanical processes.

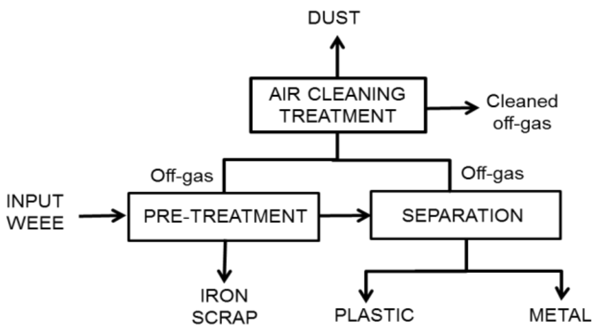

Figure 1. Schematic diagram of the plant used for the sample collections

The treatment line (Fig. 1) basically consists of a pre-treatment section, providing the size reduction of the incoming electronic waste trough shredding processes as well as the removal of iron scraps via magnetic separation. This section is then followed by a selection one, aiming at separating the metallic fraction from the plastic-based one. The treatment line is also equipped with bag filters for process air cleaning. Dust, sampled from the bag filters, was characterized by its metal content according to the aqua regia extraction procedure ISO 11466:1995.

2.2. Leaching tests

Dust was subjected to a chemical leaching process following two separate stages. During the first stage, sulfuric acid (H_2SO_4) was used as lixiviant agent. 10 g of dust were added to the leaching solution made up of 80 mL H_2SO_4 (2M) and 20 mL of hydrogen peroxide (30wt%). Operating parameters of temperature, stirring rate and leaching time were set to ambient condition, 150 rpm and 6 h, respectively. The residue from the first step was then collected and used for the second leaching stage involving thiourea ($(NH_2)_2CS$). Based on literature studies (Birloaga *et al*., 2013; Gurung *et al*., 2013), thiourea concentration, pulp density and stirring rate were selected as operating parameters to be varied simultaneously in a 2^3 full factorial design. The factors as well as the corresponding levels investigated are reported in Table 1. Temperature and leaching time were set to ambient condition and 3 h, respectively. Eight experiment combinations were run (Table 2) and the results were statistically analyzed in order to determine which effect was significant for the process (Montgomery, 1991). Each leaching experiment was done in duplicate.

Table 1. Factors and corresponding levels under investigation

Factors	Levels	
	Low (-)	**High (+)**
A: Pulp density	0.28%	2.8%
B: Thiourea concentration	0.25 M	0.5 M
C: Stirring rate	150 rpm	600 rpm

Table 2. Experimental design indicating the level of factors at each run

Run	A	B	C
1	low	low	low
2	high	low	low
3	low	high	low
4	high	high	low
5	low	low	high
6	high	low	high
7	low	high	high
8	high	high	high

2.3. Analytical methods

Liquid samples collected during each leaching test were analyzed in terms of base metals, precious metals and rare earth elements by means of inductively coupled plasma optical emission spectrometry (ICP-OES). Prior to the ICP-OES analysis, samples were filtered via nylon membrane 0.45 µm (Whatman), acidified and properly diluted. The effectiveness of the leaching process was evaluated with regard to copper and aluminum as base metals, yttrium as rare earth element and gold as precious metal. The extraction rate was obtained considering the concentration of the selected metal detected in the leaching solution and its corresponding initial concentration in the dust matrix.

3. Results and discussion

Relative high concentrations of metals were found in the dust samples. Approximately 30 g of aluminum were detected per kg of dust since this fraction is mainly composed of aluminum foils besides tiny particles and fluffy materials (Brandl *et al*., 2001). Roughly the same order of magnitude was determined for copper. Trace concentrations of precious metals and rare earth elements were also found: gold and yttrium were detected at concentrations of around 9 mg and 40 mg per kg of dust, respectively. Fig. 2 reports the metal extraction rates obtained during the first leaching step, involving sulfuric acid and hydrogen peroxide, carried out on dust samples. Almost all the aluminum was mobilized during the sulfuric acid leaching. Extraction efficiencies of around

80% and 90% were found for copper and yttrium, respectively. Conversely, no gold was extracted

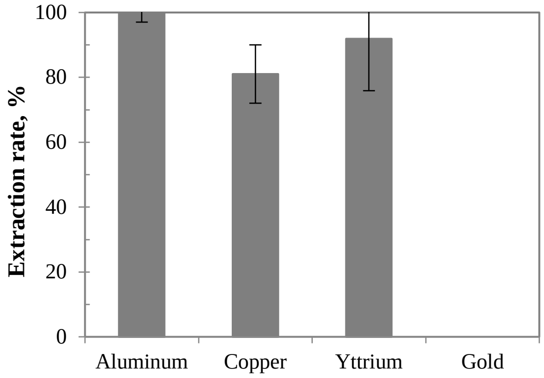

Figure 2. Extraction rates for the selected metals during sulfuric acid leaching

As metals are generally present in WEEE in their elemental form or as alloys (Tuncuk *et al*., 2012), oxidative conditions are necessary in order to dissolve these elements (Bas *et al*., 2014). The oxidation provided by the presence of hydrogen peroxide confirmed the high extraction efficiencies of base metals from electronic waste in acidic sulfate media (Deveci *et al*., 2010; Oh *et al*., 2003). Moreover, a good leaching rate was reported for yttrium. Sulfuric acid has been used for REE leaching from both native minerals and secondary materials (Jha *et al*., 2016; Tunsu *et al*., 2015). However, previous studies revealed that severe temperature conditions were necessary for the mobilization of rare earths. For instance, De Michelis *et al*. (2011) reported an extraction of yttrium at 85% by 20% w/v solid to liquid ratio, 4 N sulfuric acid concentration and 90 °C. In comparison, the present study showed higher leaching efficiencies at the same acid concentration, 10% w/v solid to liquid ratio and room temperature, which is more desirable for full scale applications. However, the less intensive temperature condition required in this work can be ascribed to the different form in which yttrium is present in the dust material under investigation (Tunsu *et al*., 2015). As reported in Fig. 2, no gold concentrations were detected in the leaching solutions as gold is not soluble in sulfuric acid (Birloaga *et al*., 2014; Oh *et al*., 2003). Gold remained, thus, in the solid residue from the first leaching step that was then subjected to a second leaching stage for gold mobilization by means of thiourea. The average extraction rates of gold reported in each leaching run using thiourea are displayed in Fig. 3 as planned by the experimental As can be seen from the graph, the best leaching rate was recorded during the run 5: around 35% of gold was mobilized when both pulp density and thiourea concentration held the low level whereas the stirring rate the high one. In the present study lower extraction efficiencies were obtained in comparison to previous literature investigations (Birloaga *et al*., 2013; Ficeriová *et al*., 2008; Gurung *et al*., 2013; Jing-ying *et al*., 2012). However, the different matrix tested as well as the consumption of thiourea by other metals in solution can be speculated to contribute to this evidence design. In order to investigate the significance of the three selected factors, the analysis of variance (ANOVA) was performed.

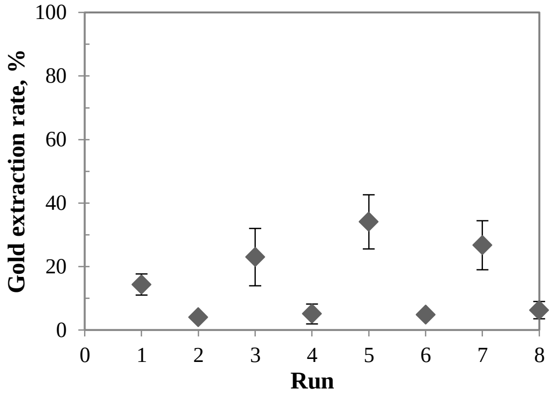

Figure 3. Average gold extraction rates during thiourea leaching

The estimated effects as well as the p-values obtained processing the data via statistical software are reported in Table 3. The “p-values” were used to determine the significant level of parameters. At a 95% confidence level (□=0.05), the effect of the factors holding a p-value<□ results statistically significant for the process response (Montgomery, 1991). In this regard, ANOVA showed that the effect of factor A, namely the pulp density, was highly significant. Moreover, factor A showed a negative effect confirming that an increasing in pulp density affects negatively the leaching process. Conversely, the effects of both factors B and C appeared not significant at least for the levels of the factors investigated in this experiment.

Table 3. Estimated effects and p-values resulting from the statistical analysis

Term	Effect	p-value
Constant	-	0,000
A	-19,475	0,001
B	0,961	0,812
C	6,346	0,143
A*B	0,306	0,940
A*C	-5,411	0,203
B*C	-3,894	0,348
A*B*C	4,104	0,324

4. Conclusions

Due to its wide-ranging composition, WEEE can represent an urban stock of secondary materials. The extensive exploitation of rare earth elements in electronic devices makes the recovery of these critical materials from WEEE particularly attractive for pursuing both economic and environmental benefits. However, the WEEE recycling chain is still in its early stages and mainly focused on the recovery of base and precious metals while low recovery rates are reported for rare earth elements. This study highlighted the opportunity to recover both valuable and critical metals from WEEE shredding dust by means of hydrometallurgical processes. In this regard, a hydrometallurgical approach developed through two separate leaching steps was found to be suitable for treating dust fraction. Around 100% of aluminum, 80% of copper and 90% of yttrium were extracted by an oxidative leaching step in sulfate media whereas 35% of gold was mobilized using thiourea, which is less toxic compared to the gold conventional lixiviant, namely cyanide. Moreover, a 2^3 full factorial design demonstrated that pulp density is the factor statistically significant for the thiourea leaching process in the range investigated. As precious metals and rare earth elements are generally conveyed during pre-treatments in dust stream destined to landfill, the proposed treatment of this fraction could avoid the losses of strategic metals, contributing furthermore to improve the quality of the residue material since the hydrometallurgical process provides the removal of certain harmful metals from the solid matrix.

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